IN THE UNITED STATE PATENT AND TRADEMARK OFFICE

In re application of :
Koji MISHIMA et al. : Docket No. 2003-1305
Serial No. 10/660,483 : Group Art Unit 1742
Filed September 12, 2003 : Examiner William T. Leader
METHOD AND APPARATUS FOR PLATING SUBSTRATE WITH COPPER

VERIFYING DECLARATION

Commissioner for Patents
P.O. Box 1450
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Sir:

I, Tetsuya Hirosawa, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of Japanese Patent Application No. H11-94943 filed on April 1, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that there statements were made with the knowledge that willful false statements and like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 26 day of June, 2006

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(NAME OF DOCUMENT) SPECIFICATION

(TITLE OF THE INVENTION) METHOD AND APPARATUS FOR PLATING SUBSTRATE WITH COPPER

(CLAIMS)

(CLAIM 1) A method for plating a substrate with copper, comprising:

bringing a substrate into contact with a pre-treatment solution containing at least one kind of organic substance which is contained in a plating solution; and

bringing the substrate into contact with the plating solution to plate the substrate.

(CLAIM 2) A method according to claim 1, further comprising performing one of removing the pre-treatment solution from the substrate and drying the substrate after said substrate is brought into contact with said pre-treatment solution before plating the substrate.

(CLAIM 3) A method according to claim 1 or 2, wherein said organic substance comprises polyether group in an organic polymer and has a concentration ranging from 10 mg/l to 10 g/l in said pre-treatment solution.

(CLAIM 4) A method according to claim 1 or 2, wherein said organic substance has a molecular weight ranging from 100 to 100,000.

(CLAIM 5) A method according to claim 1 or 2, wherein said substrate is held in contact with said pre-treatment solution for 3 to 60 seconds.

(CLAIM 6) An apparatus for plating a substrate with copper, comprising:

a device for bringing a substrate into contact with a pre-treatment solution containing at least one kind of organic substance which is contained in a plating solution; and

a device for bringing the substrate into contact with the plating solution to plate the substrate.

(CLAIM 7) An apparatus according to claim 6, further comprising:

a device for rotating the substrate so as to perform at least one of removing the pre-treatment solution from the substrate and drying the substrate before plating the substrate.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(FIELD OF THE INVENTION)

The present invention relates to a method and apparatus for separating out metal copper according to an electroplating of copper using, for example, a solution of copper sulfate in order to fill copper in fine interconnection grooves formed in a surface of a substrate such as a semiconductor wafer to produce copper interconnections on the surface of the substrate.

(0002)

(PRIOR ART)

According to a conventional electroplating for plating a substrate with copper using a solution of copper sulfate, a substrate is dipped in sulfuric acid or the like so as to be activated by the acid in a pre-treatment process outside of a plating tank, or instead of such pre-treatment process, a substrate is brought into contact with a copper sulfate solution in the plating tank without electrical current loading being made for a certain period of time (activating time), and then an electric current is supplied to separate out metal copper on the substrate.

(0003)

(PROBLEM TO BE SOLVED BY THE INVENTION)

However, the former pre-treatment process is disadvantageous in that another tank should be provided individually so as to perform the pre-treatment process, resulting in a large facility and an increased operation cost.

(0004)

On the other hand, the latter process is disadvantageous in that the plating solution and the substrate are not brought into contact with each other under constant

conditions, and hence additives such as a copper separation accelerator and a copper separation inhibitor contained in the plating solution tend to suffer initial adsorption irregularities to the surface of the substrate and activation irregularities thereof. Further, the substrate is susceptible to the specific adsorption of a component caused by a black film on a soluble anode positioned in confronting relation to the substrate. As a consequence, the metal copper is abnormally separated out locally on the surface of the substrate, causing the substrate to have a stained appearance. When the metal copper is non-uniformly and abnormally separated out locally, the crystal orientation of the copper and the thickness of the copper layer become irregular, making it difficult for the substrate to be polished to a flat finish by a chemical mechanical polishing (CMP) process after the plating process.

(0005)

According to conventional solutions to the above problems, the activating time is increased, or the substrate is rotated or the plating solution is stirred by a device known as a squeegee, whereby adsorption irregularities and activation irregularities are eliminated. However, a long activating time may result in an adverse effect on embeddability of copper into fine interconnection pattern. Other solutions referred to the above are disadvantageous in that they make the entire system complex and require a long processing time.

(0006)

It is therefore an object of the present invention to provide a method and apparatus for plating a substrate with copper which can prevent metal copper from being separated out locally on the surface of the substrate, allow a plated copper film to be easily planarized by a chemical mechanical polishing (CMP) process after the plating process, and finish the substrate to a mirror-like glossy surface with a relatively simple facility and a process.

(0007)

(MEANS FOR SOLVING THE PROBLEM)

In order to achieve the above object, according to one aspect of the present invention, there is provided a method for plating a substrate with copper, comprising: bringing a substrate into contact with a pre-treatment solution containing at least one kind of organic substance which is contained in a plating solution; and bringing the substrate into contact with the plating solution to plate the substrate.

(0008)

In the above plating method, firstly, the substrate is brought into contact with the pre-treatment solution containing the organic substance. The substrate may be brought into contact with the pre-treatment solution by directly dipping the substrate into the pre-treatment solution in a tank, by spraying the pre-treatment solution over the substrate while the substrate is being rotated in a horizontal plane at a high speed as with a spin dryer, or by supplying the pre-treatment solution by a pump into a dedicated dipping chamber in which the substrate is set at a predetermined position. When the substrate is thus brought into the pre-treatment solution, the surface of the substrate is coated with a thin film of the organic substance. An excess pre-treatment solution is preferably removed from the substrate, and then the substrate is plated with copper according to a conventional process. In this manner, metal copper is prevented from being separated out locally on the processed surface of the substrate, and the substrate is plated so as to have a mirror-like glossy appearance.

(0009)

Thereafter, it is preferable to remove the pre-treatment solution from the substrate and/or to dry the substrate for minimizing any amount of pre-treatment solution carried into the plating solution to keep better quality of the plating solution. The pre-treatment solution may be removed from the substrate by simply lowering the level of the pre-treatment solution, lifting the substrate out of the pre-treatment solution, rotating the substrate to spin off the pre-treatment solution from the substrate as with a spin dryer, rotating the substrate and applying a nitrogen gas blow to the substrate, or passing the substrate through a forced air flow such as an air blower. Further, the two processes

including removing of the pre-treatment solution and drying of the substrate may be performed successively by a single apparatus. For example, the pre-treatment solution may be sprayed over the substrate while the substrate is being rotated by a spin cleaner/dryer or the like. This method allows the substrate to contact the pre-treatment solution and also allows the pre-treatment solution to be removed from the substrate.

(0010)

The pre-treatment solution may be continuously removed from the substrate until the substrate is dried to a certain extent for thereby further minimizing the amount of pre-treatment solution carried into the plating solution. In this case, it is preferable to dry the substrate to a partly dried state with a certain moisture content, rather than fully drying the substrate.

(0011)

The inventors of the present invention assume the mechanism of the present invention, though it is not fully elucidated, as follows. Firstly, the organic substance used in the present invention, which is contained in the plating solution, is known to be effective in suppressing separating-out of copper for uniform electrodepositability. By coating the surface of the substrate with the thin layer of the organic substance in advance, separating-out of copper over the substrate in its entirety is suppressed, and any abnormal separating-out of copper is prevented. This effect remains the same after the substrate is dried to a certain extent.

(0012)

Secondly, since the organic substance is one of components contained in the plating solution, when the substrate is immersed in the plating solution, the organic substance serves to increase wettability between the plating solution and the pre-treated surface of the substrate. Even after the substrate is dried to a certain extent, this effect of the organic substance remains the same because the organic substance is eluted into the plating solution. Therefore, wetting of the surface of the substrate is improved uniformly

over its entirety, thus allowing the entire surface of the substrate to be plated uniformly and efficiently.

(0013)

Possible causes of abnormal separating-out of copper include a separation accelerator contained in the plating solution and a monovalent copper ion in a black film. In the present invention, it is presumed that the above-mentioned mechanism of the pre-treatment prevents specific attachment of these components to the substrate to thereby provide uniform deposition.

(0014)

The organic substance preferably comprises polyethers in an organic polymer for use in copper plating processes. Experiences in tests conducted by the inventors indicate that a preferable concentration of the organic substance in the pre-treatment solution is in the range of 10 mg/l to 10 g/l and a preferable molecular weight is in the rang of 100 to 100,000. The organic substance may be a copolymer or a block polymer such as polyethylene glycol, polypropylene glycol, polyvinyl alcohol, ethoxy-naphthol, propoxy-naphthol, ethoxy-phenol, propoxy-phenol, polyoxyethylene polyoxypropylene block polymer, ethoxy-nonylphenol, carboxymethylcellulose, or polyethylene proplylene glycol.

(0015)

The substrate and the pre-treatment solution containing the organic substance may be held in contact with each other for a period of time sufficient to cause the pre-treatment solution to contact the entire surface of the substrate. If the period of time were too long, the current supplying layer (underlying metal) would be chemically damaged. Thus, usually, the period of time is selected in the range from 3 to 60 seconds. If the pre-treatment solution containing the organic substance is strongly alkaline, then the hydrolysis of the organic substance tends to progress. If the acidity of the pre-treatment solution is too strong, then the copper of the current supplying layer is liable to be etched. For this reason, the pH of the pre-treatment solution is preferably in the range of 2 to 9.

(0016)

Another aspect of the present invention is to provide an apparatus for plating a substrate with copper, comprising a device for bringing a substrate into contact with a pre-treatment solution containing at least one kind of organic substance which is contained in a plating solution, and a device for bringing the substrate into contact with the plating solution to plate the substrate. A pre-treatment solution tank and a plating solution tank may be individually provided, or a single tank may be used. In a case of using separate tanks, it is preferable that these tanks are disposed close to each other and a transfer mechanism is provided so as to quickly transfer a substrate between these tanks. In a case of using a single tank, it is preferable to provide supply paths through which the pre-treatment solution and the plating solution are supplied separately, and to provide discharge paths for replace the solution in the tank. There may be provided a device for spraying the pre-treatment solution to the substrate while rotating the substrate, and then increasing speed of rotation of the substrate to thereby successively removing the solution and/or drying the substrate.

(0017)

The apparatus may further include, in addition to the processing tank and the plating tank, a loading and/or unloading unit for loading and/or unloading substrates, a transferring device for transferring substrates, and a cleaning unit for cleaning substrates, so that substrates can be loaded and unloaded in a clean condition.

(0018)

(EMBODIMENT OF THE INVENTION)

FIG. 1 is a schematic view showing a plating apparatus according to an embodiment of the present invention. The plating apparatus 1 comprises a loading unit 4 and an unloading unit 5 for loading and unloading wafer cassettes (not shown) housing substrates (not shown) such as semiconductor wafers to be processed, a delivery arm 8 and a movable delivery arm 9 for delivering substrates one at a time, a pair of coating tanks 2 for pre-treating a surface of a substrate with a pre-treatment solution, a plurality of

plating tanks 3 for plating the substrate, a cleaning unit 6 for cleaning the substrate, and a pair of rinsing and drying units 10 for rinsing and drying the substrate. Each of the coating tanks 2 and the plating tanks 3 may be a batch-type tank for processing a plurality of substrates simultaneously or an individually processing tank for processing substrates one by one. Further, each of the coating tanks 2 and the plating tanks 3 may be a dip-type tank for steadily holding a plating solution or a pre-treatment solution, or a tank for being supplied with and discharging a plating solution or a pre-treatment solution each time a plurality of substrates or a substrate is processed. The delivery arm 8 is used to handle clean substrates, and the movable delivery arm 9 is used to deliver substrates for pre-treatment.

(0019)

A process of plating a substrate (not shown) with the plating apparatus 1 will be described below with respect to a processing flow for one of the substrates. First, the wafer cassette housing substrates is set in the loading unit 4. Then, the delivery arm 8 removes a substrate from the wafer cassette, and transfers the substrate to a loading stage 7. The movable delivery arm 9 receives the substrate from the loading stage 7, and places the substrate into one of the coating tanks 2 which hold a pre-treatment solution 12. After the substrate is pre-treated by being dipped in the pre-treatment solution 12 for a certain period of time, the processed substrate is removed from the coating tank 2 by the movable delivery arm 9, and then placed into one of the plating tanks 3 holding a plating solution 13. In the plating tank 3, the substrate is electrically plated with copper.

(0020)

After the completion of the plating process, the movable delivery arm 9 removes the plated substrate from the plating tank 3, and places the substrate on the cleaning unit 6 where the substrate is cleaned in a primary cleaning stage. Then, the delivery arm 8 removes the substrate from the cleaning unit 6 and transfers the substrate to the rinsing and drying unit 10 where the substrate is cleaned in a secondary cleaning stage and then dried. The dried substrate is transferred from the rinsing and drying unit 10 to

the wafer cassette in the unloading unit 5 by the delivery arm 8. The substrates in the wafer cassette are then unloaded as the clean plated substrates, and sent to a next process such as a CMP process. The plating apparatus 1 has a plurality of the coating tanks 2 and a plurality of the plating tanks 3, and the delivery arm 8 and the movable delivery arm 9 are controlled and programmed to process substrates successively and efficiently in the coating tanks 2 and the plating tanks 3. Therefore, the plating apparatus 1 has a high operating efficiency.

(0021)

(EXAMPLES)

Examples of the plating process performed by the above plating apparatus will be described below.

The followings show pre-treatment conditions:

(1) Pre-treatment solution:

1) Polypropylene glycol (PPG, molecular weight: 400, concentration: 10 mg/l and 5 g/l);

2) Polyethylene glycol (PEG, molecular weight: 20,000, concentration: 100 mg/l and 10 g/l);

3) Mixed solution of 1) and 2) (PEG: molecular weight: 6000, concentration: 50 mg/l, PPG: molecular weight: 700, concentration: 50 mg/l).

(2) Processing time: The substrate was dipped in the pre-treatment solution for 10 seconds.

(3) Drying process:

Spin dryer (Rotational speed: 3,000 rpm. × 30 seconds, no nitrogen gas blow)

(0022)

Five substrates processed by the above pre-treatment solutions and an unprocessed substrate (comparative example) were plated in an individually processing dip-type plating tank 3.

Table 1

	Organic substances	Concentration	Appearance	CMP characteristics
Run-1	PPG	10 mg/l	Mirror finish, glossy	Good
Run-2	PPG	5 g/l	Ditto	Good
Run-3	PEG	100 mg/l	Ditto	Good
Run-4	PEG	10 g/l	Ditto	Good
Run-5	PEG + PPG	Total: 100 mg/l	Ditto	Good
Run-6	None (Comparative example)	None	Stained	Bad (lack of inter-connections)

(0023)

Furthermore, the Cu concentration on the back of the substrates was measured as reference data.

The measured Cu concentration of the unprocessed substrate was 5×10^{12} atm/cm^2, whereas the measured Cu concentration of each of the processed substrates was 5×10^{11} atm/cm^2 or lower. This result indicates that the present invention is effective to reduce a copper contamination on the back of the substrate.

(0024)

The present example was also found effective to prevent a portion of the current supplying layer where the copper film is very thin from being dissolved, resulting in the promotion of the copper deposition as a plated layer. The reason for this effect appears to be that the polymer used in the present invention also functions as an inhibitor for inhibiting the copper of the current supplying layer from being dissolved.

(0025)

FIG. 2 shows a plating apparatus according to another embodiment of the present invention. The plating apparatus in this embodiment is essentially the same as the plating apparatus 1 shown in FIG. 1 except that rotary pre-treatment units 11 are employed to pre-treat substrates. Each of the rotary pre-treatment units 11 comprises a holder mechanism for rotating a substrate, and a spray nozzle for spraying a pre-treatment solution onto the surface of the substrate. The pre-treatment solution sprayed from the spray nozzle onto the substrate is spread uniformly over the surface of the substrate while the substrate is rotated. After the supply of the pre-treatment solution is stopped, the substrate is rotated at an increased speed to remove the pre-treatment solution from the substrate and to dry the substrate in a continuous manner. Therefore, the surface of the substrate can be uniformly coated efficiently with the pre-treatment solution, dried, and plated with a desired film of copper.

(0026)

FIG. 3 shows a plating apparatus according to still another embodiment of the present invention. The plating apparatus in this embodiment has substantially the same structure as the plating apparatus shown in FIG. 2, and has a plurality of processing tanks 3, 10, 11 and a single loading and unloading unit 14 for loading and unloading a wafer cassette, all of which are disposed around a single delivery arm 8. The delivery arm 8 delivers a substrate to and from the processing tanks 3, 10, 11 and the loading and unloading unit 14. The layout of the processing tanks 3, 10, 11 and the loading and unloading unit 14 disposed around the delivery arm 8 can reduce an installation space of the plating apparatus. This plating apparatus is capable of efficiently depositing copper on a substrate and discharging it as a clean plated substrate therefrom, as with the plating apparatus 1 according to the previous embodiments.

(0027)

(EFFECT OF THE INVENTION)

According to the present invention, as described above, since copper is prevented from being abnormally separated out during copper plating, the substrate can be

uniformly plated with copper. As a result, the plated substrate can be easily polished by the subsequent chemical mechanical polishing process, and the polished substrate having a copper film can have a glossy appearance. Therefore, the yield of products can be increased, and the cost of LSI circuit fabrication can greatly be lowered. Accordingly, the method and the apparatus for plating a substrate with copper according to the present invention are highly useful and effective in the industry of semiconductor fabrication.

(BRIEF DESCRIPTION OF THE DRAWINGS)

(FIG. 1)

FIG. 1 is a schematic plan view of a plating apparatus according to an embodiment of the present invention.

(FIG. 2)

FIG. 2 is a schematic plan view of a plating apparatus according to another embodiment of the present invention.

(FIG. 3)

FIG. 3 is a schematic plan view of a plating apparatus according to still another embodiment of the present invention.

(EXPLANATION OF THE REFERENCE NUMERALS)

1 plating apparatus
2 coating tank
3 plating tank
4 loading unit
5 unloading unit
6 cleaning unit
7 loading stage
8 delivery arm
9 movable delivery arm
10 rinsing and drying unit
11 rotary pre-treatment unit

12 pre-treatment solution

13 plating solution

14 loading and unloading unit

(NAME OF DOCUMENT) ABSTRACT

(ABSTRACT)

(OBJECT) The object of the present invention is to provide a method and apparatus for plating a substrate with copper which can prevent metal copper from being separated out locally on the surface of the substrate, allow a plated copper film to be easily planarized by a chemical mechanical polishing process after the plating process, and finish the substrate to a mirror-like glossy surface with a relatively simple facility and a process.

(MEANS FOR RESOLUTION) The method for plating a substrate with copper include bringing a substrate into contact with a pre-treatment solution 12 containing at least one kind of organic substance which is contained in a plating solution 13, and bringing the substrate into contact with the plating solution to plate the substrate.

(SELECTED FIGURE) Fig. 1

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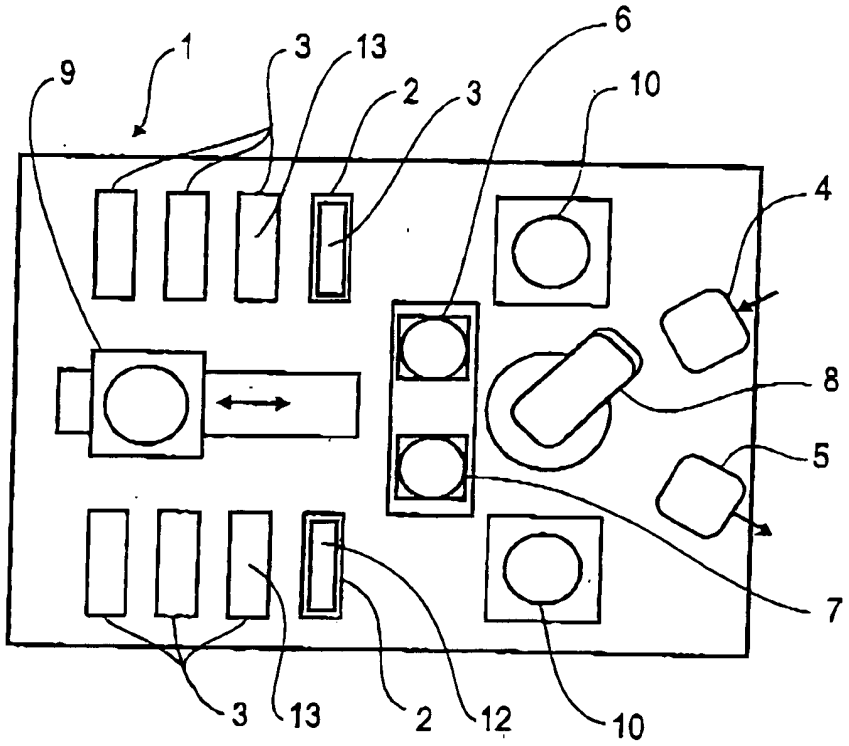
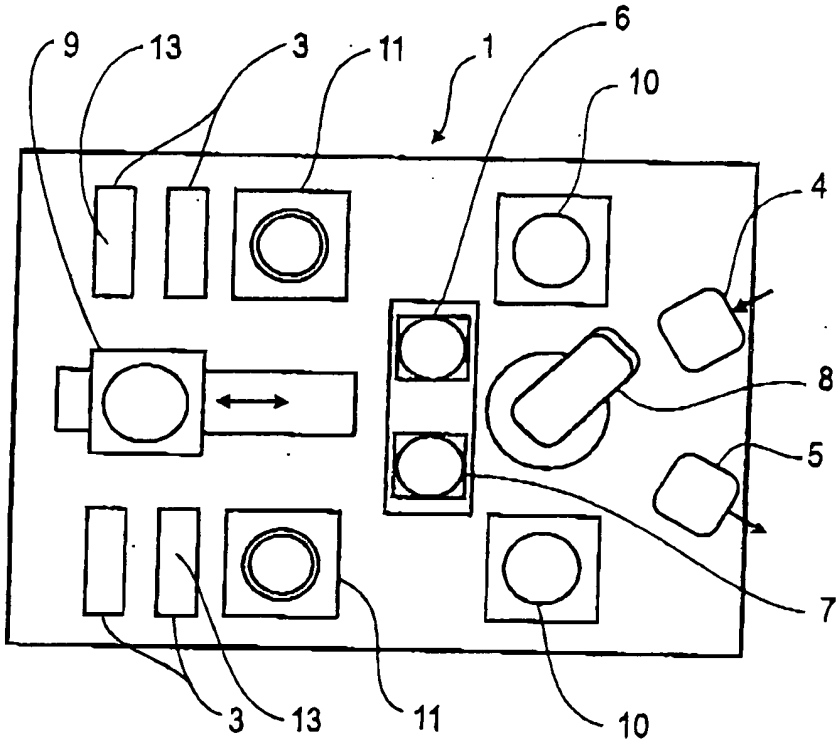
REFERENCE NUMBER=EB1888P 11-094943 1/3

(NAME OF DOCUMENT) DRAWINGS
(FIG. 1)

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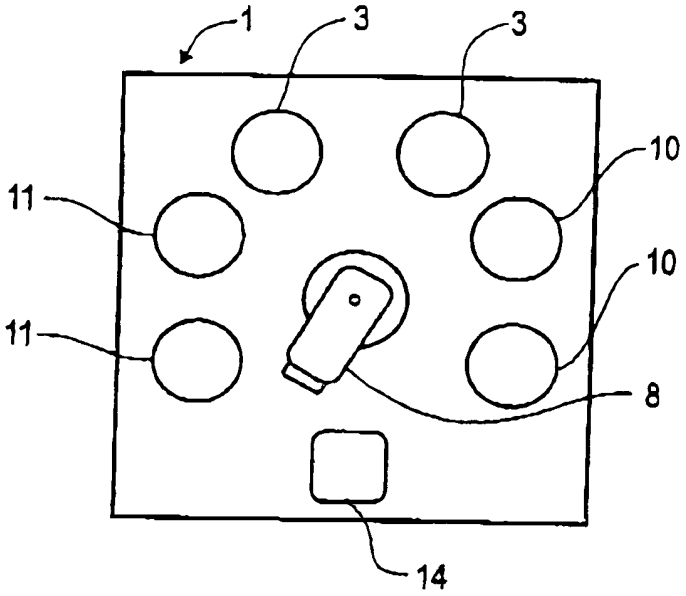
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